Electroluminescent devices using a layered organic-inorganic perovskite structure as emitter

Michael Cölle[a], Wolfgang Brütting[a] and Markus Schwoerer[a]
Masayuki Yahiro[b] and Tetsuo Tsutsui[b]

[a] Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany
[b] Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

ABSTRACT

Self-organizing layered perovskite compounds like $(C_6H_5C_2H_4NH_3)_2PbI_4$ naturally form a dielectric quantum-well structure in which semiconducting PbI_4 layers and organic $(C_6H_5C_2H_4NH_3)$ layers are alternately piled up. Due to their low-dimensional semiconductor nature they exhibit a strong absorption and sharp photoluminescence from the exciton band. In electroluminescent devices pure green emission peaking at 520nm with a very narrow half-width of about 10nm has been reported. As the organic-inorganic layered structure has promising properties for EL-devices, we investigated two- and three layer structures using this perovskite as emitter material in combination with additional hole and electron injection layers. To get more insight into electrical properties and electroluminescence-mechanisms of this material, temperature dependent current-voltage-luminance characteristics have been measured, showing an increasing onset-voltage for current flow from 2.6V at room temperature to about 8.8V at 80K. Electroluminescence is detected at temperatures below 150K with onset voltages of about 13V. At liquid nitrogen temperature efficiencies of 0.7cd/A at 100cd/m^2 and 1.8cd/A at 10,000 cd/m^2 are obtained.

Keywords: Multilayer device, hole transport layer, layered perovskite, organic-inorganic composite, self-organization

1. INTRODUCTION

Perovskites, in general, are compounds with the chemical formula AMX_3. This simple structure consists of a network of corner-sharing MX_6 octahedra, where the M atom is typically a metal cation and X is an anion (e.g. O^{2-}, Cl^-, Br^-, I^-), with the appropriate charge to balance the A and M cations. One example is $BaTiO_3$, that is known for its ferroelectric properties. Oriented layered perovskite materials with the chemical formula A_2MX_4 belong to the family of high-temperature superconductors (e.g. La_2CuO_4). These structures consist of layer with high conductivity separated by so called modulation layers.

Organic chemistry offers considerably more flexibility in controlling molecular parameters, thus replacing the inorganic modulation layer with an organic layer offers a high potential designing materials for the particular application desired. As for electroluminescent (EL) devices, the hybridization of organic and inorganic semiconductors is expected not only to permit wide-range selection of emitter and carrier transport materials, but also to provide a new approach to create high performance EL devices taking advantages of organic and inorganic semiconductors.

The organic-based layered R-(alkylammonium) metal (II) tetra halide $(RNH_3)_2PbX_4$ (R stands for the organic compound or chromophore and X for the halogen atom e.g. Cl, Br or I) self-organize into a superlattice quantum well structure: a two-dimensional inorganic semiconductor layer of lead tetrahalide PbX_4 is sandwiched between organic alkylammonium layers of RNH_3 as shown in figure 1, thus two-dimensional semiconductor layers of lead iodide PbI_4 and organic ammonium dielectic layers of RNH_3 are alternately piled up.[1] As determined by x-ray diffraction, the layered structure of spin-coated or evaporated thin films is oriented parallel to the film plane.[2–4]

The perovskites form stable excitons with large binding energy due to their low dimensionality. In addition to the dimension of the inorganic perovskite layer (the confinement and thus the binding energy decreases with increasing

Further author information:
Michael Cölle: E-mail: michael.coelle@uni-bayreuth.de

dimension) the binding energy of the exciton can be controlled by variation of the dielectric constant of the organic layer.

Thus, this perovskite compounds have enormous variety, which may be utilized for studying the physics in these quantum well materials. A variety of phenomena like luminescence,[5–7] third harmonic generation,[8] electroabsorption,[9] four-wave mixing,[10] phosphorescence[11,12] and electroluminescence[13] have been reported and are under investigation.

Some of these compounds exhibit intense exciton absorption and photoluminescence from the exciton band even at room temperature. Moreover, the spectral characteristics of the layered perovskites can easily be modified by replacement of the organic alkylammonium layer, the metal and the halide. This feature provides the tuneability of emission color and the electrical properties.[14,15] In addition, the perovskites possess good film processability. By using the conventional spin-coating method, optically high quality thin films can be obtained. From the above mentioned features, these perovskite materials are expected to be a promising thin film material for light-emitting devices.[16,13,17]

In this paper we focus on one particular material of these perovskites with iodine as halogen atom and R= phenylethylen: bis (phenethylammonium) tetraiodoplumbate, $(C_6H_5C_2H_4NH_3)_2PbI_4$ (abbreviated as PhE-PbI_4). After a brief review on the most important features of this particular material for EL applications, we present temperature dependent photoluminescence spectra (section 3) and I-V-EL-characteristics of two layer devices. Then, two-layer devices and three-layer devices with Copper(II) phthalocyanine (CuPc) and poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) (here abbreviated as PEDOT) as hole injection layer will be compared at liquid nitrogen temperature.

2. EXPERIMENTAL AND SAMPLE FABRICATION

2-Phenyl-ethyl-ammonium-iodide $(C_6H_5C_2H_4NH_3)I$ was synthesized, Lead (II) iodide (PbI_2) was purchased form Aldrich and purified by recrystallization. $(C_6H_5C_2H_4NH_3)I$ and PbI_2 were dissolved in N,N-dimethylformamide

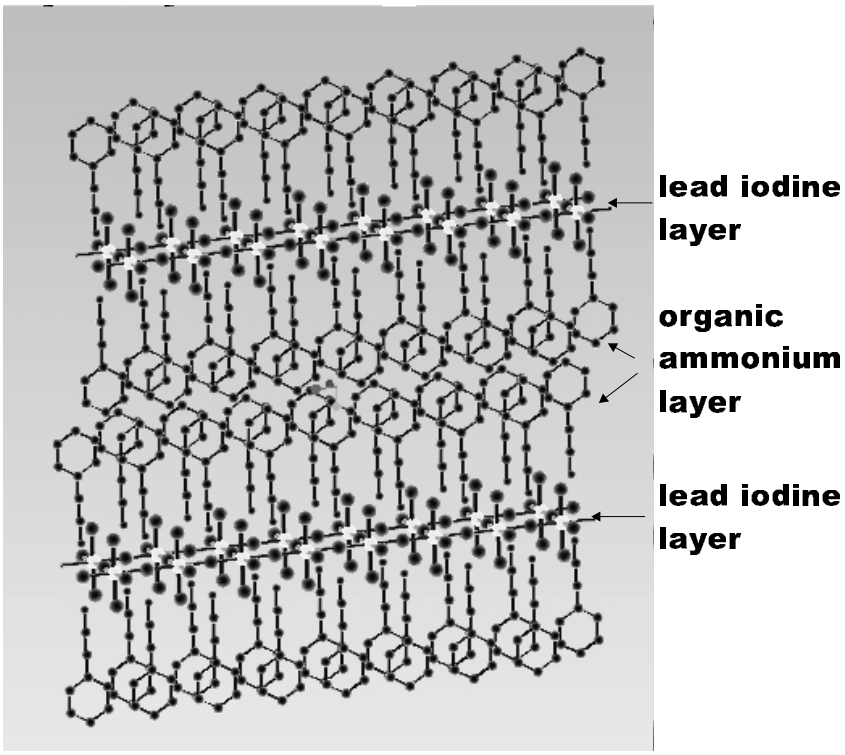

Figure 1. Schematic structure of the $(C_6H_5C_2H_4NH_3)_2PbI_4$ layered quantum well. PbI_6 octahedra share four corners forming two-dimensional layers separated by two organic layers of $(C_6H_5C_2H_4NH_3)_2$.

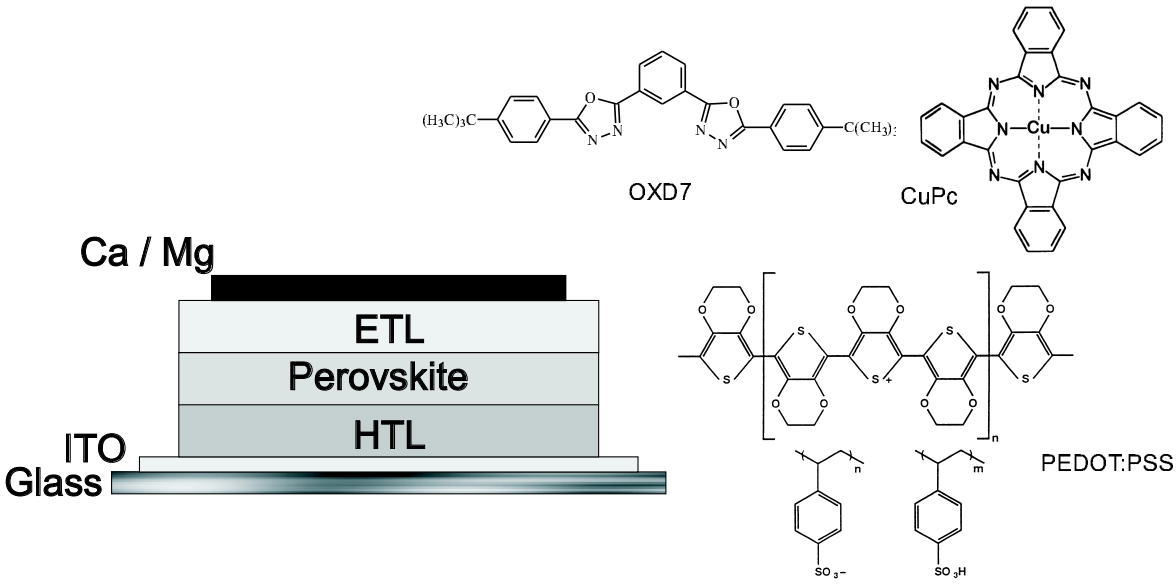

Figure 2. Device structure of the organic-inorganic heterostructure EL devices using $(C_6H_5C_2H_4NH_3)_2PbI_4$ (PhE-PbI_4) spin coated perovskite film and molecular structures of the organic materials used as injection layers. We used CuPc or PEDOT:PSS as hole transport layer (HTL), OXD7 as electron transport layer (ETL) and the perovskite PhE-PbI_4 as emitter material.

$HCON(CH_3)_2$ (DMF). The stoichiometric molar ratio of lead iodine to organic ammonium iodide was 1:2. Transparent and homogeneous solutions with a concentration of 10% have been used for spin-coating.

Purification of the substrate turned out to be very important to achieve good and homogeneous films. ITO substrates were cleaned with acetone in ultrasonic bath and with isopropanol. After that, the surface was etched in oxygen plasma for 15 minutes.

PEDOT (Baytron P from Bayer AG) and perovskite layer have been spin-coated at 3000rpm onto the ITO substrate (conductivity: $100\Omega/\square$) under ambient conditions. Spin-coating was carried out at room temperature in the case of PEDOT and at 100^oC for the perovskite solution because of the high boiling point of DMF (153^oC).

The thickness of these films was measured with a Dektak 3030 ST. The film thickness of PEDOT and Perovskite layer were about 40nm and 60nm respectively. CuPc and ODX7 with a thickness of 20nm and 40nm respectively as well as the calcium and magnesium cathode have been vacuum deposited at a pressure of 10^{-6}mbar. The device structure and molecular structure of these materials are shown in figure 2.

A Perkin Elmer (Lambda 2 UV-VIS spectrometer) was used for the absorption spectra at room temperature. Current-voltage (I-V) characteristics of the devices were recorded using a computer controlled source-measure unit (Keithley 236). Simultaneously with the current the flux of emitted light was measured using a calibrated Si photodiode and an electrometer (Keithley 617). Emission spectra were obtained by a liquid nitrogen cooled charge coupled device (CCD) detector coupled to a monochromator (Princeton Instruments, Solar). For photoluminescence measurements an UV-LED with a wavelength of 370nm was used to excite the samples. The devices were placed in a cryostate and measured under inert atmosphere. The Commission Internationale d'Eclairage (CIE) color coordinates and luminance (cd/m^2) were taken by a spot photometer (Minolta CS-100).

3. OPTICAL PROPERTIES OF PHE-PEROVSKITE FILM

In general the emission spectra of organic LEDs have a large full width at half maximum (FWHM) of about 50 to 100nm. This is due to both inhomogenous broadening and the presence of a vibronic progression. For displays (e.g. full-color red-green-blue (RGB) displays), however, saturated and pure colors are needed. Recently there are a lot of activities to make efficient devices with a narrow FWHM emission by using metal-organic compounds.[18,19] Hong

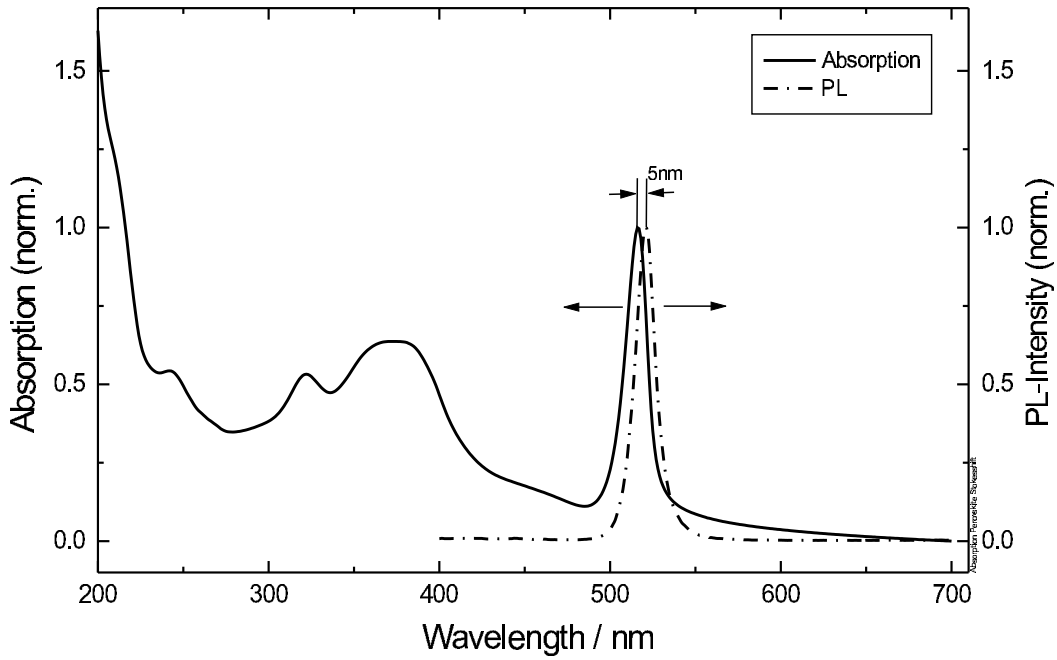

Figure 3. Absorption (solid line) and photoluminescence spectrum (dotted line) of spin-coated PhE-PbI_4 film at room temperature. The photoluminescence spectrum has a very narrow full width at half maximum of about 10nm and a small Stokes shift of about 5nm.

et al.[16] reported on electroluminescence of a single crystal of PhE-Pb_2I_7 and Era et al. created a two-layer organic-inorganic electroluminescent device, analogous to the organic LEDs but using PhE-PbI_4 as an emitter material. The hetero-structure device consisted of an indium tin oxide (ITO) anode, a PhE-PbI_4 emitter layer, an oxadiazole derivative (OXD7) electron transport layer covered by a MgAg cathode. For these devices a brightness of more than 10.000cd/m^2 at liquid nitrogen temperature has been reported.[13]

A characteristic feature of this particular perovskite material is the narrow exiton-band with FWHM of 10 to 15nm and its very small Stokes shift of only a few nanometers. In Figure 3 the absorption spectrum and the photoluminescence spectrum of a spin coated PhE-Perovskite film with a thickness of 40nm are shown. The EL spectrum of the device corresponds well to the photoluminescence spectrum of the PhE-PbI_4 film: the peak of the emission is at about 520nm and has a very narrow FWHM of only about 10nm.

Figure 4 shows the temperature dependent photoluminescence spectrum of a perovskite layer with a thickness of 40nm from room temperature down to liquid nitrogen temperature. The photoluminescence intensity increases strongly with decreasing temperature. The dominant peak at 524nm is assigned to the free exciton. A slight red shift of the photoluminescence peak from 524nm at 300K to 527nm at 78K is discernible. This slightly positive temperature coefficient has been explained by a weak electron lattice coupling in this compound.[20]

The Bohr radius of the exciton has been calculated to be slightly larger than the distance of the lead ions, thus the exciton is Wannier like. Its binding energy is high (about 220meV) because of the two dimensional confinement of this quantum well structure and the dielectric confinement of the exciton in the inorganic perovskite layer ($\epsilon_{PbI_4} = 6.1$) between two organic layers with a low dielectric constant ($\epsilon_{PhE} = 2.4$).[20,21]

At temperatures below 150K a second band is discernible that is related to the bound exciton.[20] The energetic difference between these two bands is about 20meV. At temperatures above 150K thermal activation is sufficient to free the bound exciton thus only the free exciton band is observed in the photoluminescence spectrum at room temperature. As one can see in figure 4 photoluminescence intensity is increasing with decreasing temperature, suggesting an increasing photoluminescence quantum efficiency. In order to estimate the value for temperature dependent photoluminescence quantum efficiency, we first measured the value at room temperature using an inte-

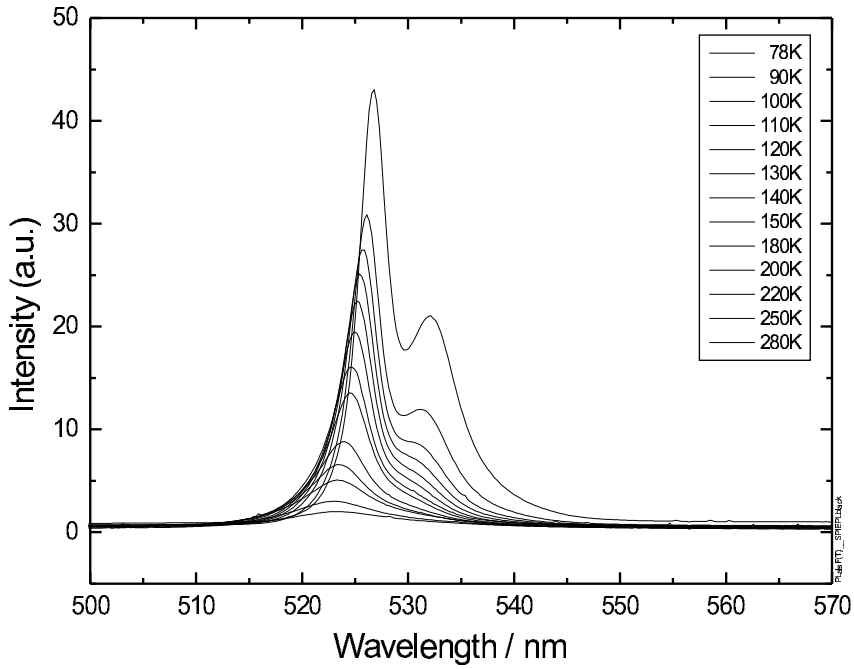

Figure 4. Temperature dependent photoluminescence-spectra of a spin coated PhE-PbI_4 film with a thickness of 40nm. Photoluminescence intensity is increasing with decreasing temperature.

grating sphere. As the strong excitation beam and the much weaker photoluminescence signal have to be measured simultaneously the error is relatively high. Going on the assumption that the absorption of the film is constant with decreasing temperature, one can calculate the photoluminescence quantum efficiency at low temperatures. The values at room temperature are about 1-2% and the factor between room temperature and 78K is about 24 thus the quantum efficiency at 78K is estimated to be between 24-48%. Calculation of the factor at low temperature is very sensitive to the choice of the baseline to subtract the background noise. These values are in agreement with the reported external quantum efficiency of 0.9% for two layer PhE-PbI_4 EL-devices[22] but have to be considered as a rough estimation.

4. ELECTRICAL DEVICE CHARACTERISTICS

Figure 5 shows temperature dependent I-V-EL-characteristics of a ITO/PhE-PbI_4/OXD7/Ca device. At room temperature current onset voltage is about 2.6V. Intense photoluminescence is observed at room temperature though no EL was observed. At 150K and lower temperatures, bright EL occurs. The EL-spectrum is similar to the photoluminescence spectrum and can be assigned to the free exciton state. Current onset of the devices is shifted to 8.8V at 80K. In order to compare the EL characteristics, investigations of the two and three layer devices have all been made at a temperature of 80K to avoid degradation.

Injection or transport layers are used to facilitate carrier injection as well as for blocking carriers injected from the opposite electrode. This leads to an accumulation of the carriers at the organic-organic interface, shifting the recombination zone away from the metal electrodes. In organic light emitting diodes (OLEDs) hole injection layers (eg. consisting of CuPc, PEDOT or NPB) are commonly used to increase the device performance. Beside of the balance factor for injection of holes and electrons, low (onset-) voltages are desirable for a good power efficiency of LEDs,[23] as well as high currents for bright EL.

For the perovskite devices presented here, PEDOT and CuPc were used as hole injection layer. Figure 6 shows the I-V-characteristic of PhE-PbI_4/OXD7 and the three layer devices CuPc/PhE-PbI_4/OXD7 and PEDOT/PhE-PbI_4/OXD7 respectively. There is a remarkable difference between the onset voltages. Whereas for the two layer

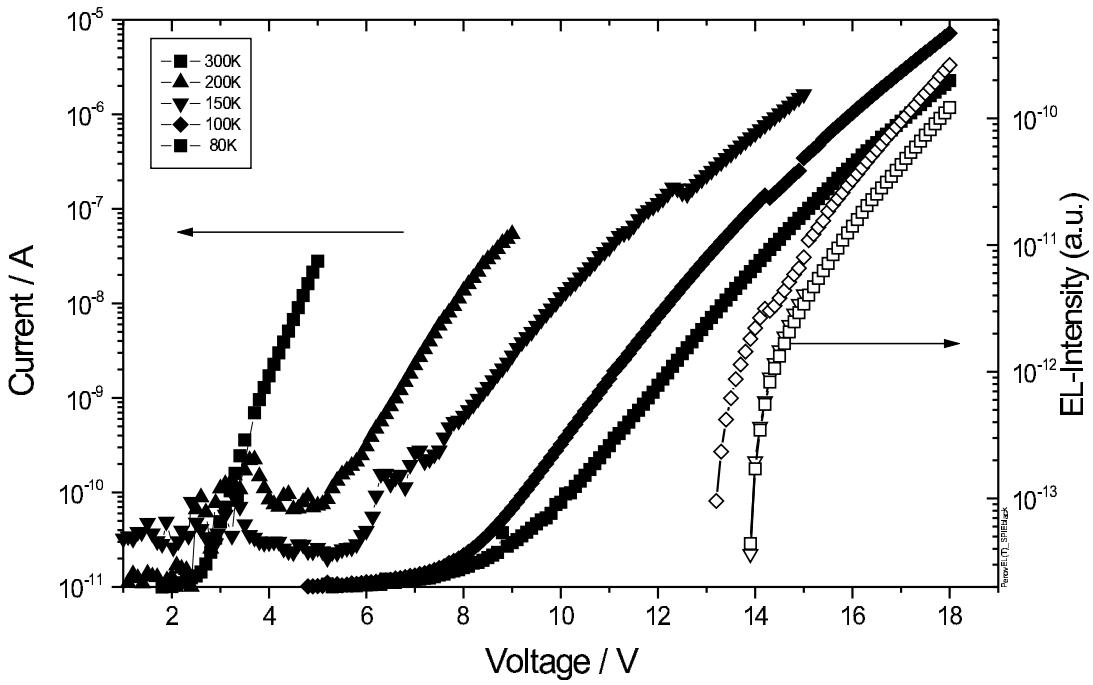

Figure 5. Temperature dependent I-V-EL-characteristics of ITO/PhE-PbI_4/OXD7/Ca devices. Current: solid symbols, electroluminescence (EL): open symbols.

device and the CuPc-device EL starts at a voltage of 12V, for the PEDOT-device it is nearly half of this value. The onset voltage is reduced to 7V.

The high leakage current of the PEDOT/PhE-PbI_4/OXD7 device at voltages between 0V and 10V is symmetric at negative bias. It is due to the device geometry used and the relatively high conductivity of the spin coated PEDOT-layer that is in contact with both electrodes on the substrate. For devices fabricated in this geometry with PEDOT layer we often observe this behaviour, thus it seems not to be related to processes within the device.

The main difference is the current flow through the devices. At a voltage of 18V the difference between the two layer device and the PEDOT/PhE-PbI_4/OXD7 structure is more than three orders of magnitude. Brightness is correlated to current flow through the device. At 18V the brightness of the PEDOT/PhE-PbI_4/OXD7 device is also more than two orders of magnitude higher. The brightness of this three layer device is up to 10.000cd/m^2 with an efficiency of 1.8cd/A.

Figure 7 shows the schematic energy diagram of the materials used for these OLEDs. Values are taken from literature, but they differ somehow for the same material (e.g. for CuPc from 4.8eV[24] to 5.2eV[25] . The HOMO-level of PEDOT and CuPc are similar thus the big difference in current and brightness can not be explained only by these small differences of the HOMO levels. Onset voltages for the CuPc-devices and the two-layer devices are similar and the CuPc-layer seems not to improve the device performance notably.

A difference might be due to the interface at the perovskite layer. CuPc is not soluble in DMF, but the surface of the PEDOT-layer might be macerated due to the spin-coating process of the perovskite layer and form a new interface structure or slight mixture of the materials at the interface. Due to the fast growing process of the crystal structure during the spin-coating process, there can be some strain in the film, thus a slightly rough surface with little flaws is formed.

In figure 8 EL-spectra of the different devices are shown: in all devices the active layer is the perovskite layer with a pure green colour (x=0.16, y=0.8). The FWHM for all devices is about 15nm except of the PEDOT-device. Its EL-spectrum has a slightly different shape and is a little broader with a FWHM of about 20nm. The inset also demonstrates the big advantage of using a pure green emitter like this: in combination with standard red and blue emitters a very large range of colours is possible (area of the triangle). The points for red R(x=0.61, y=0.342), blue

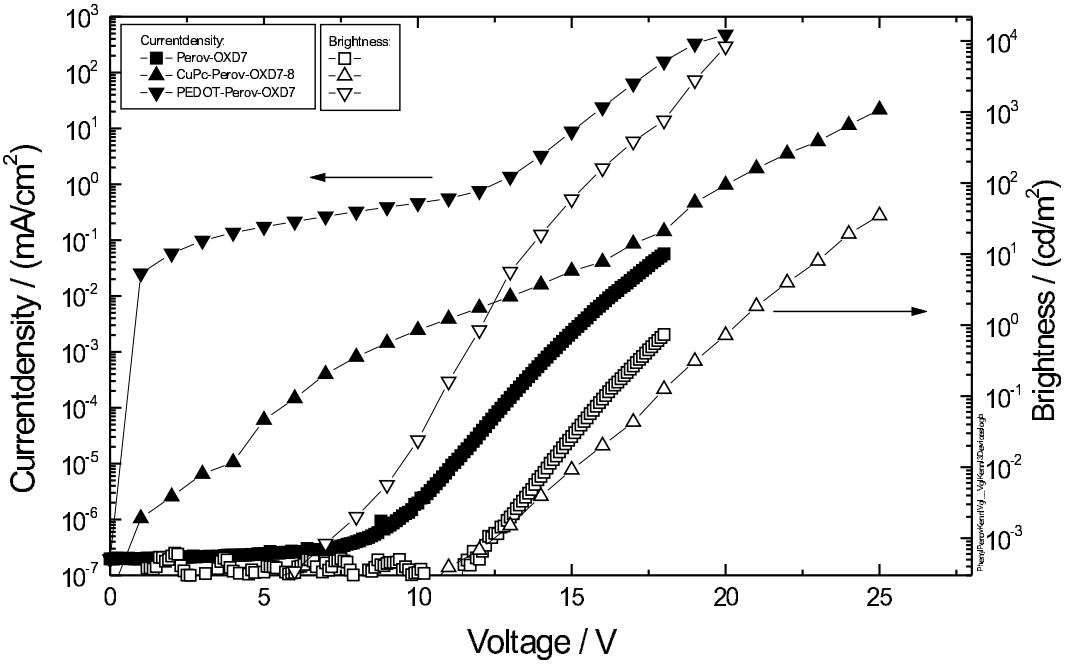

Figure 6. Current density (solid symbols) and brightness (open symbols) of two- and three-layer devices as a function of applied voltage.

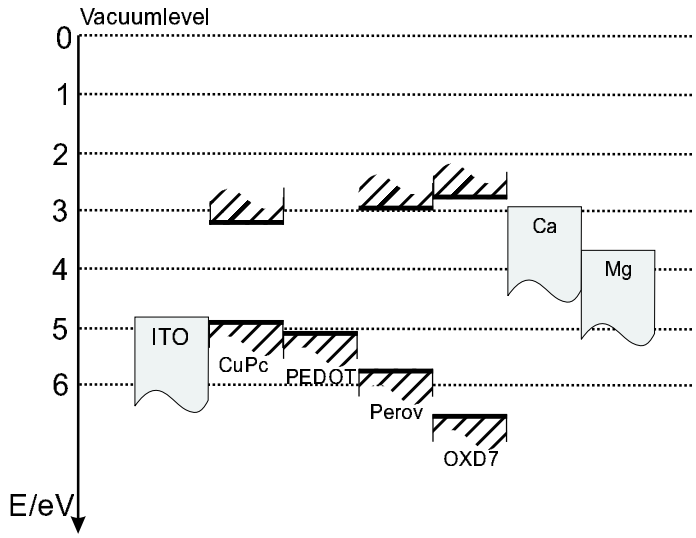

Figure 7. Energy diagram of the materials used for the organic LEDs.

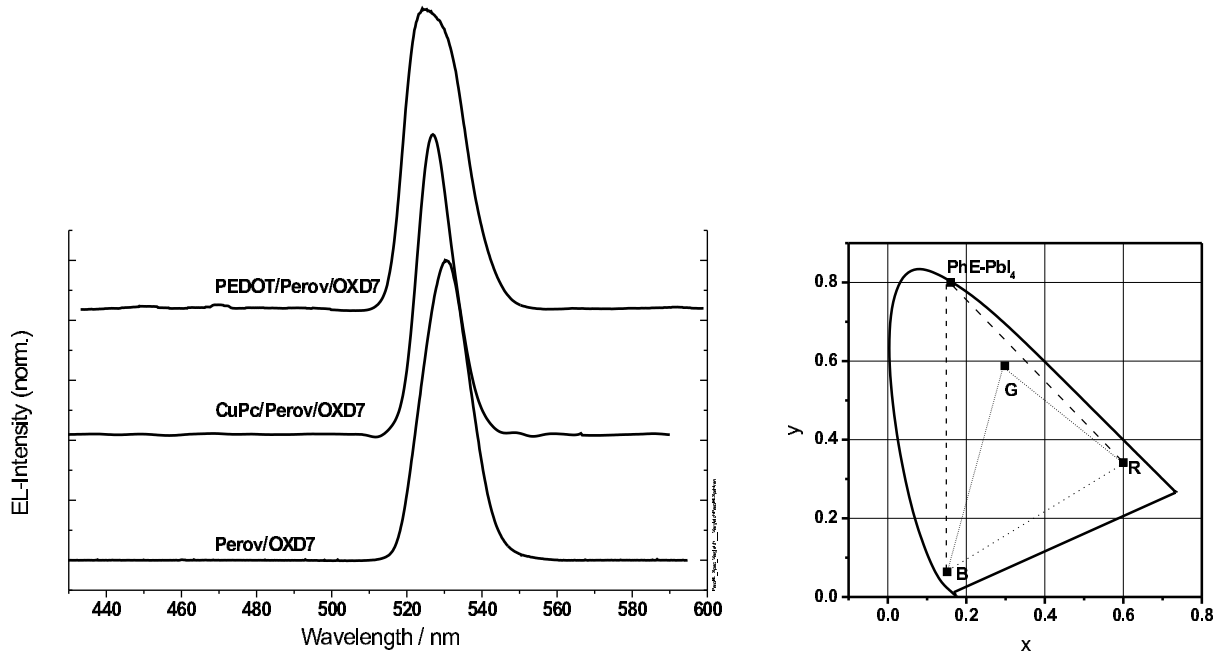

Figure 8. EL-spectra of the devices used in this study. The emission of all devices is clearly originated from the PhE-PbI_4-layer. The inset shows the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates of PhE-PbI_4. R, B and G are the phosphor CIE coordinates for red, blue and green of a commercial computer monitor. The triangle formed with standard red and blue demonstrates the large range of colours that can be achieved with a pure green emitter like this.

B(x=0.15, y=0.064) and green G(x=0.298, y=0.588) marked in the inset are the phosphor CIE coordinates of a commercial computer monitor.[26]

It is reported, that for polymer LEDs an incorporated PEDOT:PSS film between the ITO electrode and the emissive layer leads to a marked reduction of the anode barrier height at the hole-injecting interface, and accounts for a variety of improvements brought about by the PEDOT insertion, namely: the increase of luminescence efficiency, the reduction of the turn-on voltage and the increase of the device lifetime.[27] In our three layer perovskite devices with PEDOT layer, we observed the same improvements. Reasons for polymer LEDs are protection from chemical interaction with ITO[28] and reduction of short formation due to smoothing of the ITO surface.[29] Chemical doping of the PEDOT:PSS was observed and used for photovoltaic cells.[30] Although there seems to be a similarity to the influence of using PEDOT as hole injection layer in polymer LEDs, the reason for the improvement of the performance in the PEDOT-perovskite-devices still has to be clarified.

Summarizing we presented temperature dependent photoluminescence spectra of PhE-PbI_4 films and I-V-EL characteristics of two layer perovskite LEDs. We compared three layer devices with the perovskite PhE-PbI_4 as emitter material. PEDOT and CuPc were used as hole injection layer. Whereas the use of CuPc did not result in remarkable improvement of the device performance, incorporating PEDOT:PSS film between the ITO and the PhE-PbI_4 layer caused reduction of the turn-on voltage, increased the device lifetime and led to higher current flow through the device associated with higher brightness.

ACKNOWLEDGMENTS

We thank the Bayreuther Institut für Makromolekülforschung (BIMF) for financial support.

REFERENCES

1. D. Mitzi, C. Feild, W. Harrison, and A. Guloy, "Conducting tin halides with a layered organic-based perovskite structure," *Nature* **369**, p. 467, 1994.
2. M. Era, K. Maeda, and T. Tsutsui, "PbBr-based layered perovskite containing chromophore-linked ammonium molecule as an organic layer," *Chem. Lett.* **1**, p. 1235, 1997.
3. J. Calabrese, N. Jones, R. Harlow, N. Herron, D. Thorn, and Y. Wang, "Preparation and characterization of layered lead halide compounds," *J. Am. Chem. Soc.* **113**, p. 2328, 1991.
4. M. Era, T. Hattori, T. Taira, and T. Tsutsui, "Self-organized growth of PbI-based layered perovskite quantum well by dual-source vapor deposition," *Chemistry of Materials* **9**, p. 8, 1997.
5. G. Papavassiliou, A. Patsis, D. Lagouvardos, and I. Koutselas, "Spectoscopic studies of $(C_{10}H_{21}NH_3)_2PbI_4$, $(CH_3NH_3)(C_{10}H_{21}NH_3)_2Pb_2I_7$, $(CH_3NH_3)PbI_3$ and similar compounds," *Synth. Met.* **55-57**, p. 3889, 1993.
6. N. Kitazawa, "Excitons in two-dimensional layered perovskite compounds: $(C_6H_5C_2H_4NH_3)_2Pb(Br,I)_4$ and $(C_6H_5C_2H_4NH_3)_2Pb(Cl,Br)_4$," *Materials Science and Engineering B* **49**, p. 233, 1997.
7. T. Ishihara, J. Takahashi, and T. Goto, "Exciton state in two-dimensional perovskite semiconductor (C10H21NH3)2PbI4," *Solid State Communications* **69**, p. 933, 1989.
8. C. Xu, T. Kondo, H. Sakakura, K. Kumata, Y. Takahashi, and R. Ito, "Optical third harmonic generation in layered perovskite-type material $(C_{10}H_{21}NH_3)_2PbI_4$)," *Solid State Communications* **79**, p. 245, 1991.
9. C. Xu, S. Fukuta, H. Sakakura, T. Kondo, R. Ito, Y. Takahashi, and K. Kumata, "Anomalous electro-absorption in the low-temperature phase of $(C_{10}H_{21}NH_3)_2PbI_4$)," *Solid State Communications* **77**, p. 923, 1991.
10. J. Ishi, M. Mizuno, H. Kunigita, K. Ema, S. Iwamoto, S. Hayase, T. Kondo, and R. Ito, "Third-order optical nonlinearity due to excitons and biexcitons in a self-organized quantum-well material $(C_6H_{13}NH_3)_2PbI_4$)," *J. Nonl. Opt. Phys. Mat.* **7**, p. 153, 1998.
11. M. Era, K. Maeda, and T. Tsutsui, "Enhanced phosphorescence from naphthalene-chromophore incorporated into lead bromide-based layered perovskite having organic-inorganic superlattice structure," *Chem. Phys. Lett.* **296**, p. 417, 1998.
12. M. Braun, *Selbstorganisierte organische Schichten in Bleihalogenid-Kristallen.* PhD thesis, University of Stuttgart, 1999.
13. M. Era, S. Morimoto, T. Tsutsui, and S. Saito, "Organic-inorganic heterostructure electroluminescent device using a layered perovskite semiconductor $(C_6H_5C_2H_4NH_3)_2PbI_4$)," *Appl. Phys. Lett.* **65**, p. 676, 1994.
14. D. Mitzi, "Synthesis, structure, and properties of organic-inorganic perovskites and related materials," *Prog. Inorg. Chem.* **48**, p. 1, 1999.
15. T. Ishihara, "Optical properties of Pb-based inorganic-organic perovskites," in *Optical Properties of Low-Dimensional Materials*, T. Ogawa and Y. Kanemitsu, eds., pp. 288–339, World Scientific, Singapore, 1995.
16. X. Hong, T. Ishihara, and A. Nurmikko, "Photocunductivity and electroluminescence in lead iodide based natural quantum well structures," *Solid State Communications* **84**, p. 657, 1992.
17. M. Era, S. Morimoto, T. Tsutsui, and S. Saito, "Electoluminescent device using two dimensional semiconductor $(C_6H_5C_2H_4NH_3)_2PbI_4$) as an emitter," *Synth. Met.* **71**, p. 2013, 1995.
18. C. Adachi, M. A. Baldo, and S. R. Forrest, "Electroluminescence mechanisms in organic light emitting devices employing a europium chelate doped in a wide energy gap bipolar conducting host," *J. Appl. Phys.* **87**, p. 8049, 2000.
19. M. Baldo, D. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. Thompson, and S. Forrest, "Highly efficient phosphorescent emission from organic electroluminescent devices," *Nature* **395**, p. 151, 1998.
20. T. Ishihara, J. Takahashi, and T. Goto, "Optical properties due to electonic transitions in two-dimensional semiconductors $(C_nH_{2n+1}NH_3)_2PbI_4$," *Phys. Rev. B* **42**, p. 11099, 1990.
21. X. Hong, T. Ishihara, and A. Nurmikko, "Dielectric confinement effect on excitons in PbI_4-based layered semiconductors," *Phys. Rev. B* **45**, p. 6961, 1991.
22. T. Hattori, T. Taira, M. Era, T. Tsutsui, and S. Saito, "Highly efficient electoluminescence from a heterostructure device combined with emissive layered-perovskite and an electron-transporting organic compound," *Chem. Phys. Lett.* **254**, p. 103, 1996.
23. T. Tsutsui and K. Yamamato, "Evaluation of true power luminous efficiency from experimental luminance values," *Jpn. J. Appl. Phys.* **38**, p. 2799, 1999.

24. G. Parthasarathy, P. Burrows, V. Khalfin, V. Kozlov, and S. Forrest, "A metal-free cathode for organic semiconductor devices," *Appl. Phys. Lett.* **72**, p. 2138, 1998.
25. I. Hill and A. Kahn, "Organic semiconductor heterointerfaces containing bathocuproine," *J. Appl. Phys.* **86**, p. 4515, 1999.
26. Apple Computer, "iMac hardware, CIE phosphor settings," 2000.
27. T. Brown, J. Kim, R. Friend, F. Cacialli, and R. D. W. Feast, "Built-in electroabsorption spectroscopy of polymer light-emitting diodes incorporating a doped poly(3,4- ethylene dioxythiophene) hole injection," *Appl. Phys. Lett.* **75**, p. 1679, 1999.
28. A. Berntsen, P. van de Weijer, S. Croonen, C. Liedenbaum, and J. Vleggaar, "Stability of polymer light-emitting diodes," *Philips Research* **51**, p. 511, 1998.
29. S. Karg, J. Scott, J. Salem, and M. Angelopoulos, "Increased brightness and lifetime of polymer leds with polyaniline anodes," *Synth. Met.* **80**, p. 111, 1996.
30. A. Arias, M. Granström, D. Thomas, K. Petritsch, and R. Friend, "Doped conducting-polymer-semiconducting-polymer interfaces: Their use in organic photovoltaic devices," *Phys. Rev. B* **60**, p. 1854, 1999.